The Reaction of Pyrroles with Trimethylhalosilanes-Dialkyl Sulfoxides

Franco Bellesia, Franco Ghelfi, Romano Grandi,
Ugo Maria Pagnoni and Adriano Pinetti*

Dipartimento di Chimica dell'Università. Via Campi, 183,
I-41100 Modena, Italy

Received November 9, 1992

Pyrroles are powerful nucleophiles in the reaction with dialkyl sulfoxides and trimethylchlorosilane (TMCS) or trimethylbromosilane (TMBS), affording sulfonium salts or halo derivatives, generally in good yields.

J. Heterocyclic Chem., **30**, 617 (1993).

Trimethylchlorosilane/dimethyl sulfoxide has been widely used for the preparation of α-chloroketones and sulfonium salts from carbonylic compounds [1a], and of β-chlorothioethers from alkenes [1b]. A variety of sulfoxides and trimethylhalosilanes was subsequently examined using indole and its homologues as substrates [2]. On increasing the size of the alkyl groups of the sulfoxide and/or shifting from chloride to the more nucleophilic bromide ion, the product distribution can be rationalised by the attack of the halogen electrophilic reagent species **B**, derived from the conversion of the sulfur electrophile **A** [3] (Scheme 1).

While the treatment of indoles with TMCS/DMSO preferentially affords halogenated products [2], preliminary experiments on pyrroles showed the predominating formation of sulfonium salts. To further investigate this different behaviour and because of the importance of pyrrole sulfonium salts as building blocks in drug synthesis [4], we planned a more extensive study of the reaction of a number of *C*- and *N*-alkylated pyrroles with a variety of sulfoxides and halosilanes.

Scheme 1

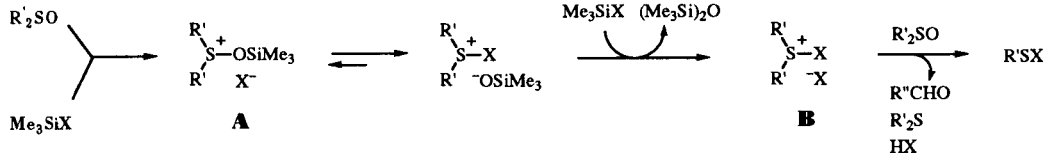
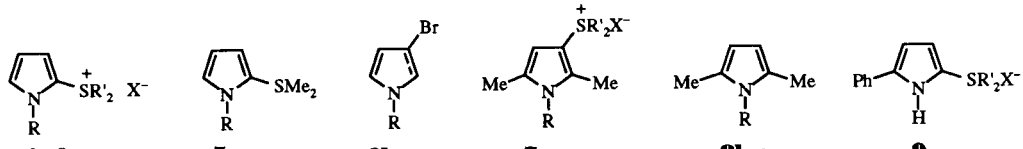
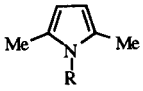
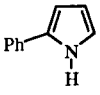


Table 1

Products and Yields (in parentheses) from the Reaction of Pyrroles with Trimethylhalosilanes-dialkyl Sulfoxides



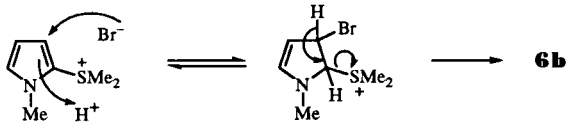
Substrate		R	Reagent System	Me_2SO \TMCS $R'_2 = Me_2$	Et_2SO \TMCS $R'_2 = Et_2$	$(CH_2)_4SO$ \TMCS $R'_2 = (CH_2)_4$	Bu_2SO \TMCS $R'_2 = Bu_2$	Me_2SO \TMBS $R'_2 = Me_2$
1		**a** H		**4a** (69)	**4a** (65)	**4a** (85)	**4a** (60)	**4a** (65)
		b Me		**4b** (69)	**4b** (68)	**4b** (55)	**4b** (73)	**4b** (52) **6b** (16)
		c Ph		**5c** (80)	**5c** (76)	**5c** (82)	**5c** (81)	**6c** (50)
2		**a** H		**7a** (62)	**7a** (62)	**7a** (53)	**7a** (60)	**7a** (66)
		b Me		**7b** (75)	**7b** (72)	**7b** (67)	**7b** (50)	**8b** (55)
		c Ph		**7c** (62) **8c** (12)	**7c** (66) **8c** (15)	**7c** (40) **8c** (18)	**7c** (55) **8c** (9)	**8c** (65)
3				**9** (65)	**9** (71)	**9** (58)	**9** (60)	**9** (55)

Results and Discussion.

The reactions are carried out at 0° in acetonitrile, conditions which give smoother conversions and higher yields.

Pyrrole (**1a**) and *N*-methylpyrrole (**1b**) afford C_2-sulfonium salts **4a** and **4b** with all the reagents reported in Table 1. On using TMBS/DMSO, pyrroles are generally more reactive than indoles [2], giving sulfonium salts. The formation, in relative low yield, of the 3-bromo derivative **6b** from **1b** may be easily explained by the process [5] reported in Scheme 2 through an initial proton catalysis; [2-(*N*-methylpyrrolyl)]dimethylsulfonium bromide (**4b**, X = Br, R' = Me) partially (40%) converts in the reaction medium into **6b**, with 2-thiomethyl-*N*-methylpyrrole (30%) as the side product. The amount of **6b** rises on increasing the reaction times, most likely owing to the formation of hydrobromic acid (Scheme 1). Accordingly, on treating the same substrate **4b** (X = Br, R' = Me) with hydrobromic acid, **6b** is obtained in good yields (75%). *N*-Phenylpyrrole (**1c**) affords no sulfonium salt but only halo derivatives (at C_2, **5c** with TMCS and at C_3 **6c** [6] with TMBS), regardless of the sulfoxide involved, probably since the aromatic conjugation reduces its reactivity. Accordingly, in parallel runs, *N*-(*p*-ethoxyphenyl)pyrrole affords sulfonium salts in 15-25% yields besides the expected halogenated products, whereas only small amounts of 2-chloro or 3-bromo derivatives are obtained from *N*-(*p*-nitrophenyl)pyrrole, more than 50% of starting material being recovered. In parallel runs, *N*-acetylpyrrole gives no reaction at all.

Scheme 2



4b

2,5-Dimethylpyrroles **2a-c** afford C_3-3 sulfonium salts **7a-c** (Table 1) with TMCS and each sulfoxide. Unlike 1-phenylpyrrole (**1c**) which gives only halo derivatives **5c** and **6c**, 2,5-dimethyl-1-phenylpyrrole (**2c**) affords the 3-sulfonium salts, with only minor amounts of the 3-chloro derivative; this is probably explained by the relatively twisted position in **2c** of the phenyl and pyrrole rings [7]. On using TMBS and DMSO the sulfonium salt **7a** is obtained

Table 2

Physical and Spectroscopic Data of 2-Pyrrolyldialkylsulfonium Salts

Product	Mp °C (solvent)	Formula MS (m/z)	Elemental Analysis (Calcd./Found) C	H	N	S	^{1}H NMR (deuterium oxide) (δ)
4a R'$_2$ = Me$_2$	153	$C_6H_{10}ClNS$	44.03	6.16	8.56	19.59	3.10 (6H, *s*), 6.40 (1H, dd), 7.00 (1H, dd), 7.25
X = Cl	AcMe	113 [a]	44.20	6.51	8.65	19.60	(1H, dd)
4a R'$_2$ = Et$_2$	135-138	$C_8H_{14}ClNS$	50.12	7.36	7.31	16.72	0.80 (6H, t), 3.60 (4H, dq), 6.46 (1H, dd), 7.20
X = Cl	AcMe	127 [a]	50.55	7.51	7.24	16.75	(1H, dd), 7.49 (1H, dd)
4a R'$_2$ = (CH$_2$)$_4$	135-138	$C_8H_{12}ClNS$	50.65	6.38	7.38	16.90	2.37 (4H, bm), 3.21 (4H, dq), 6.46 (1H, dd), 6.87
X = Cl	AcMe	153 [b]	50.52	6.51	7.44	16.95	(1H, dd), 7.20 (1H, dd)
4a R'$_2$ = Bu$_2$	56-61	$C_{12}H_{22}ClNS$	58.16	8.95	5.65	12.94	0.70 (6H, bm), 1.35 (8H, bm), 3.45 (4H, t), 6.31
X = Cl	AcOMe	155 [a]	58.30	9.05	5.48	12.84	(1H, dd), 6.97 (1H, dd), 7.25 (1H, dd)
4a R'$_2$ = Me$_2$	87-89	$C_6H_{10}BrNS$	34.63	4.84	6.73	15.40	3.10 (6H, *s*), 6.40 (1H, dd), 7.00 (1H, dd), 7.25
X = Br	AcMe	113 [a]	34.53	4.53	6.62	15.52	(1H, dd)
4b R'$_2$ = Me$_2$	120-125	$C_7H_{12}ClNS$	47.32	6.91	7.88	18.04	3.05 (6H, *s*), 3.75 (3H, *s*), 6.28 (1H, bd), 6.95
X = Cl	AcMe	127 [a]	47.25	7.13	7.98	18.23	(2H, m)
4b R'$_2$ = Et$_2$	96-99	$C_9H_{16}ClNS$	52.54	7.84	6.81	15.58	0.82 (6H, bt), 3.20 (4H, q), 3.70 (3H, *s*), 6.25
X = Cl	AcMe	141 [a]	52.48	7.96	6.68	15.73	(1H, dd), 6.91 (2H, m)
4b R'$_2$ = (CH$_2$)$_4$	112-117	$C_9H_{14}ClNS$	53.06	6.93	6.88	15.74	2.37 (4H, m), 3.60 (4H, bt), 3.72 (3H, *s*), 6.26
X = Cl	AcOMe	167 [b]	53.24	7.02	6.68	15.85	(1H, bd), 6.93 (2H, m)
4b R'$_2$ = Bu$_2$	55-61 dec	$C_{13}H_{24}ClNS$	59.63	9.24	5.35	12.24	0.75 (6H, bt), 1.20-1.65 (8H, bm), 3.41 (4H,
X = Cl	AcOMe	195 [a]	59.77	9.45	5.61	12.17	bq), 3.70 (3H, *s*), 6.26 (1H, dd), 6.89 (2H, m)
4b R'$_2$ = Me$_2$	83-88	$C_7H_{12}BrNS$	37.85	5.44	6.31	14.43	3.05 (6H, *s*), 3.75 (3H, *s*), 6.28 (1H, bd), 6.95
X = Br	AcMe	127 [a]	37.98	5.61	6.24	14.58	(2H, m)
9 R'$_2$ = Me$_2$	126-127	$C_{12}H_{16}ClNS$	59.61	6.67	5.79	13.26	3.22 (6H, *s*), 6.63 (1H, m), 7.07 (1H, m), 7.35-
X = Cl	AcMe	192 [a]	59.91	6.77	5.65	13.10	7.62 (5H, m), 7.85 (1H, b)
9 R'$_2$ = Et$_2$	105-106	$C_{14}H_{20}ClNS$	62.32	7.47	5.19	11.88	0.80 (6H, bt), 3.21 (4H, dq), 6.70 (1H, m), 7.31
X = Cl	AcOMe	205 [a]	62.21	7.34	5.11	12.06	(1H, m), 7.35-7.65 (5H, m)
9 R'$_2$ = (CH$_2$)$_4$	85-89 dec	$C_{14}H_{18}ClNS$	62.79	6.77	5.23	11.97	2.37 (4H, bm), 3.60 (4H, bm), 6.58 (1H, d), 7.22
X = Cl	AcOMe	233 [b]	62.66	6.51	5.35	12.06	(1H, dd), 7.30-7.60 (5H, m)
9 R'$_2$ = Bu$_2$	waxy oil	$C_{18}H_{26}ClNS$	66.74	8.09	4.32	9.90	0.70 (6H, bt), 1.35 (8H, bm), 3.45 (4H, t), 6.58
X = Cl		231 [a]	66.79	8.15	4.36	9.99	(1H, m), 7.15 (1H, m), 7.30-7.65 (5H, m)
9 R'$_2$ = Me$_2$	65-70	$C_{12}H_{16}BrNS$	50.36	5.63	4.89	11.20	3.22 (6H, *s*), 6.63 (1H, m), 7.07 (1H, m), 7.35-
X = Br	AcMe	191 [a]	50.44	5.65	4.91	11.23	7.62 (5H, m)

[a] m/z = M$^+$ -R'X [b] m/z = M$^+$ -HCl.

only from **2a**, whereas *N*-substituted 2,5-dimethyl substrates afford the 3-bromo derivatives **8b,c** together with some dibromo derivative.

In parallel runs, 2-phenylpyrrole (**3**) [8] gives the corresponding 2-(5-phenylpyrrolyl)dialkyl sulfonium salts **9** generally in good yields.

Table 3
Physical and Spectroscopic Data of 3-(2,5-dimethylpyrrolyl)dialkyl Sulfonium Salts

Product	Mp °C (Solvent)	Formula MS (m/z)	Elemental Analysis (Calcd./Found) C	H	N	S	^{1}H NMR (deuterium oxide) (δ)
7a $R'_2 = Me_2$ X = Cl	115-118 AcOMe	$C_8H_{14}ClNS$ 141 [a]	50.12 50.00	7.36 7.45	7.31 7.28	16.72 16.82	2.14 (3H, s), 2.25 (3H, s), 2.92 (6H, s), 6.20 (1H, q)
7a $R'_2 = Et_2$ X = Cl	110-115 AcOMe	$C_{10}H_{18}ClNS$ 155 [a]	54.65 54.80	8.26 8.26	6.37 6.15	14.59 14.71	1.13 (6H, t), 2.12 (3H, s), 2.25 (3H, s), 3.30 (4H, m), 6.08 (1H, bs)
7a $R'_2 = (CH_2)_4$ X = Cl	115-117 AcMe	$C_{10}H_{16}ClNS$ 181 [b]	55.16 55.09	7.41 7.47	6.43 6.53	14.72 14.71	2.12 (3H, s), 2.27 (3H, s), 2.35 (4H, bm), 3.50 (4H, bm), 6.08 (1H, bs)
7a $R'_2 = Bu_2$ X = Cl	62-67 AcMe	$C_{14}H_{26}ClNS$ 183 [a]	60.95 60.80	9.50 9.45	5.08 5.25	11.62 11.65	0.72 (6H, bt), 1.35 (8H, bm), 2.05 (3H, s), 2.12 (3H, s), 3.51 (4H, m), 5.98 (1H, s)
7a $R'_2 = Me_2$ X = Br	121-124 AcOMe	$C_8H_{14}BrNS$ 141 [a]	40.69 40.65	5.98 5.89	5.93 5.95	13.57 13.37	2.14 (3H, s), 2.25 (3H, s), 2.92 (6H, s), 6.20 (1H, q)
7b $R'_2 = Me_2$ X = Cl	169-170 AcMe	$C_9H_{16}ClNS$ 155 [a]	52.54 52.61	7.84 7.89	6.81 6.87	15.58 15.42	2.15 (3H, s), 2.27 (3H, s), 2.95 (6H, s), 3.40 (3H, s), 6.32 (1H, s)
7b $R'_2 = Et_2$ X = Cl	120-125 AcMe	$C_{11}H_{20}ClNS$ 169 [a]	56.51 56.48	8.62 8.65	5.99 6.12	13.71 13.65	1.15 (6H, bt), 2.15 (3H, s), 2.27 (3H, s), 3.35 (4H, dq), 3.51 (3H, s), 6.33 (1H, s)
7b $R'_2 = (CH_2)_4$ X = Cl	135-137 AcMe	$C_{11}H_{18}ClNS$ 195 [b]	57.00 57.15	7.83 7.95	6.04 6.00	13.83 13.90	2.15 (3H, s), 2.27 (3H, s), 2.40 (4H, m), 3.40 (3H, s) 3.45 (4H, m), 6.30 (1H, s)
7b $R'_2 = Bu_2$ X = Cl	100-103 AcOMe	$C_{15}H_{28}ClNS$ 197 [a]	62.15 62.05	9.73 9.91	4.83 4.88	11.06 11.21	0.75 (6H, bt), 1.20-1.50 (8H, m), 2.08 (3H, s), 2.18 (3H, s), 3.40 (3H, s), 3.50 (4H. m), 6.25 (1H, bs)
7b $R'_2 = Me_2$ X = Br	135-138 AcMe	$C_9H_{16}BrNS$ 155 [a]	43.21 43.11	6.45 6.32	5.60 5.41	12.81 12.97	2.14 (3H, s), 2.25 (3H, s), 2.92 (6H, s), 6.20 (1H, q)
7c $R'_2 = Me_2$ X = Cl	40-45 AcMe	$C_{14}H_{18}ClNS$ 217 [a]	62.79 62.71	6.77 6.78	5.23 5.36	11.97 12.08	1.88 (3H, s), 2.02 (3H, s), 2.97 (6H, s), 6.42 (1H, bs), 7.35 (5H, m)
7c $R'_2 = Et_2$ X = Cl	41-47 AcMe	$C_{16}H_{22}ClNS$ 231 [a]	64.95 65.00	7.49 7.56	4.73 4.96	10.84 10.57	1.15 (6H, t), 1.90 (3H, s),2.03 (3H, s), 3.40 (4H, m), 6.40 (1H, s), 7.10-7.55 (5H, m)
7c $R'_2 = (CH_2)_4$ X = Cl	35-38 AcOMe	$C_{16}H_{20}ClNS$ 257 [b]	65.40 65.32	6.86 6.99	4.77 4.71	10.91 11.06	1.90 (3H, s), 2.02 (3H, s), 2.30 (4H, m), 3.50 (4H, m), 6.35 (1H, s), 7.10-7.55 (5H, m)
7c $R'_2 = Bu_2$ X = Cl	waxy	$C_{20}H_{30}ClNS$ 259 [a]	68.25 68.41	8.59 8.37	3.98 4.00	9.11 9.07	0.75 (6H, bt), 1.35 (8H, bm), 1.81 (3H, s), 1.98 (3H, s), 3.45 (4H, m), 6.27 (1H, bs), 7.35 (5H, m)
7c $R'_2 = Me_2$ X = Br	50-53 AcMe	$C_{14}H_{18}BrNS$ 217 [a]	53.85 53.99	5.81 6.03	4.49 4.47	10.27 10.20	1.88 (3H, s), 2.02 (3H, s), 2.97 (6H, s), 6.42 (1H, bs), 7.35 (5H, m)

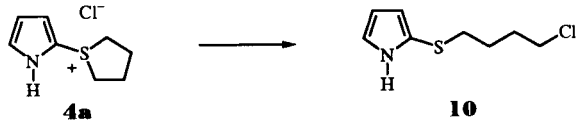
[a] m/z = M^+ -R'X [b] m/z = M^+ -HCl.

Table 4
Physical and Spectroscopic Data of Isolated Halopyrroles

Product	Bp °C	Formula MS (M^+)	Elemental Analysis (Calcd./Found) C	H	N	^{1}H NMR (deuterium oxide) (δ)
6b X = Br	110-112/15	C_5H_6BrN 160	37.53 37.43	3.78 3.90	8.75 8.70	3.51 (3H, s), 6.10 (1H, dd), 6.45 (1H, dd), 6.50 (1H, dd)
5c X = Cl	130-134/1	$C_{10}H_8ClN$ 178	67.62 67.48	4.54 4.60	7.89 7.74	6.25 (2H, m), 6.80 (1H, dd), 7.50 (5H, bs)
6c X = Br	131-135/0.1	$C_{10}H_8BrN$ 222	54.08 54.18	3.63 3.50	6.31 6.42	6.35 (1H, d), 6.95 (1H, bd), 7.05 (1H, bs), 7.30 (5H, bs)
8b X = Br	109-115/2	$C_7H_{10}BrN$ 188	44.71 44.55	5.36 5.32	7.45 7.31	2.15 (6H, bs), 3.55 (3H, s), 5.75 (1H, d), 7.60 (1H, bs)
8c X = Cl	135-136/0.1 dec	$C_{12}H_{12}ClN$ 206	70.07 70.23	5.88 6.01	6.81 6.75	1.98 (6H, s), 5.92 (1H, bs), 7.10-7.60 (5H, m)
8c X = Br	140-144/0.1 dec	$C_{12}H_{12}BrN$ 250	57.62 57.55	4.84 4.96	5.60 5.76	1.98 (3H, s), 2.00 (3H, d), 6.12 (1H, q), 7.05-7.65 (5H, m)

On increasing the reaction times the sulfonium salts are dealkylated to thioalkylpyrroles [9]; the isolated sulfonium salt **4a** affords 2-(4-chloro-*n*-butylthio)pyrrole (**10**) in 60% yield when heated in DMSO (Scheme 3) [10].

Scheme 3



4a **10**

On delaying the substrate addition after the complete evolution of the reagent system (Scheme 1), halo derivatives are obtained in good yields and without side-products [11], even when sulfonium salts would have been expected. The use of butyl sulfoxide and TMCS on *N*-phenylpyrrole appears to be the only exception, affording, besides a 20% of the expected 2-chloro derivative, a nearly equimolecular mixture of 2- and 3-*n*-butylthio-*N*-phenylpyrroles in a 60% total yield. The low reactivity of the substrate very likely allows a further reagent evolution to *n*-butansulfenyl chloride, affording [12] sulfur derivatives.

Furan and thiophene afford mono- and di-halogenation in low yields and an extended polymerisation with all the reported reagent systems. No reaction at all is observed from pyrazoles and imidazoles, the only recovered products being the corresponding hydrochlorides and hydrobromides.

EXPERIMENTAL

Melting and boiling points are uncorrected. The gc-ms data have been recorded on a HP 5989 mass spectrometer. The ^{1}H nmr spectra are recorded on a Bruker FP80 and a Varian XL200 spectrometers and measured from TMS as internal standard. The DMSO has been dried by distillation over calcium hydride. Substrates **2a-c** have been prepared according to literature methods [13]. Other solvents or substrates were standard grade commercial products.

General Reaction Procedure.

In a 100 ml round bottom flask fitted with magnetic stirrer and protected from moisture, the appropriate pyrrole (5 mmoles) is dissolved in acetonitrile [14] (30 ml). The solution is cooled down to 0° with an ice/water bath, then dialkyl sulfoxide and trimethylhalosilane (5.5 mmoles each) are quickly added. The reaction mixture, which soon turns dark brown, is allowed to reach the room temperature and is checked (tlc) for the disappearance of the substrate. When the reaction is complete (tlc monitoring), the solvent is removed *in vacuo*. The residue is treated with methyl acetate (or acetone when the bulkier sulfoxides are used), the precipitate is filtered off and recrystallised to give the sulfonium salts. The mother liquors are then evaporated and the residue is chromatographed on silica gel (*n*-hexane/diethyl ether); the collected fractions afford the halo derivatives pure enough for characterisation. Chloro- and bromopyrroles soon darken in the air and in chloroform solution [15].

Delayed Addition of the Substrates.

The dialkyl sulfoxides (5 mmoles) are dissolved in acetonitrile (20 ml) in a round bottomed flask and thermostatted at 0°. The TMCS (5 mmoles) is quickly added with magnetic stirring. After 10 minutes the substrate (2.4 mmoles) in acetonitrile (5 ml) is added, and the mixture allowed to reach the room temperature. When the reaction is complete (tlc monitoring), the mixture is diluted with water, extracted with methylene chloride, and dehydrated over sodium sulfate. After the *in vacuo* evaporation of the solvent, the brown residue is chromatographed on silica gel (*n*-hexane/diethyl ether 4:1), the chloro derivatives are obtained (65-80% yield) sufficiently pure for characterisation. By using TMBS bromo derivatives are obtained in the same way, although with lower yields. With TMCS/dibutyl sulfoxide, besides the expected 2-chloro derivative **5c**, (20% yield), 1-phenylpyrrole affords 2-butylthio-1-phenylpyrrole in 31% yield; ^{1}H nmr (deuteriochloroform): δ 0.95 (3H, bt), 1.55 (4H, bm), 2.52 (2H, bt), 6.25 (2H, m), 6.80 (1H, m), 7.40 (5H, m); ms: M$^+$ 231.

3-Butylthio-1-phenylpyrrole is also obtained from the above reaction in 28% yield; ^{1}H nmr (deuteriochloroform): δ 0.95 (3H, bt), 1.55 (4H, bm), 2.52 (2H, bt), 6.40 (1H, m), 7.12 (1H, m), 7.38 (1H, m), 7.40 (5H, m); ms: M$^+$ 231.

3-Bromo-*N*-methylpyrrole (**6b**).

[2-(*N*-Methylpyrrolyl)]dimethylsulfonium bromide (**4b**, R′ = Me, X = Br) (250 mg, 1.12 mmoles) is dissolved in acetonitrile (10 ml) and concentrated hydrobromic acid (48%, 0.25 ml, 2.24 mmoles) is added to the solution. The mixture is thermostatted at 60° and after 1 hour the sulfonium salt disappears (tlc monitoring). After dilution with water (50 ml), extraction with methylene chloride (3 x 30 ml) and dehydration over sodium sulfate, the *in vacuo* removal of the solvent affords a dark brown oily residue which is chromatographed on silica gel (diethyl ether/*n*-hexane 1:4) to give **6b** (146 mg, 75% yield) and 2-thiomethyl-*N*-methylpyrrole (56.5 mg, 33% yield); ms: M$^+$ 127; ^{1}H nmr (deuteriochloroform): δ 2.20 (3H, s), 3.70 (3H, s), 5.98 (1H, dd), 6.20 (1H, dd), 6.90 (1H, dd).

2-(4-Chloro-*n*-butylthio)pyrrole (**10**).

Tetramethylene(2-pyrrolyl)sulfonium chloride (**4a**, R′$_2$ = $(CH_2)_4$, X = Cl) (350 mg, 1.85 mmoles) is dissolved in anhydrous DMSO (10 ml) and heated to 60° until all the salt disappears and a tlc spot (Rf = 0.4, silica gel and diethyl ether/*n*-hexane 1:4 as eluant) reaches its maximum. The solution is cooled, diluted with water (100 ml) and extracted with methylene chloride (2 x 50 ml). The organic layers, dried on sodium sulfate and distilled *in vacuo*, afford an oily residue that is purified by preparative tlc to a 95% pure product **10**, (229 mg, 66% yield) as an oil, Kp$_5$ 140-155° dec; ms: 190 (M$^+$); ^{1}H nmr (deuteriochloroform): δ 1.78 (4H, bm), 2.70 (2H, t), 3.52 (2H, t), 6.15 (1H, bd), 6.35 (1H, ds) and 6.83 (1H, bs).

Acknowledgements.

Financial support from the C.N.R. and the Ministero della Ricerca Scientifica (Rome) are gratefully acknowledged. We thank Professor A. Rastelli (Modena) for helpful discussion.

REFERENCES AND NOTES

* To whom correspondence should be directed.

[1a] F. Bellesia, F. Ghelfi, R. Grandi and U. M. Pagnoni, *J. Chem. Res. (S)*, 426 (1986); [b] F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, *ibid.*, 238 (1987).

[2] F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, *J. Chem. Res. (S)*, 182 (1989).

[3] G. E. Wilson, *Tetrahedron*, 2597 (1982).

[4] F. Franco, R. Greenhouse and J. M. Muchowsky, *J. Org. Chem.*, **47**, 1682 (1982).

[5] R. Carson and N. M. Davis, *J. Org. Chem.*, **46**, 839 (1981).

[6] D. J. Chadwick and S. T. Hodgson, *J. Chem. Soc., Perkin Trans. 1*, 93 (1983).

[7] This is probably the reason for the similar behaviour of 1-(4-nitrophenyl)- and 1-(4-ethoxyphenyl)-2,5-dimethylpyrrole, which affords the expected sulfonium salts (60-71%) with small amounts (8-12%) of halo derivatives.

[8] Th. Severin and H. Poehlman, *Chem. Ber.*, **110**, 490 (1977); F. Momicchioli and A. Rastelli, *J. Mol. Spectros.*, **23**, 310 (1967); F. Momicchioli and G. del Re, *J. Chem. Soc. (B)*, 675 (1969).

[9] F. Bellesia, F. Ghelfi and U. M. Pagnoni, *J. Chem. Res. (S)*, 24 (1987); C. J. M. Stirling, Sulfonium Salts in S. Oae, Organic Chemistry of Sulfur, Plenum Press, N.Y., 1977, p 492.

[10] Ethylbutyl(2-pyrrolyl)sulfonium chloride, obtained from pyrrole **1a** by reaction with TMCS and butyl ethyl sulfoxide [^{1}H nmr (DMSO-d_6): δ 0.70 (3H, bt), 1.05 (3H, t), 1.35 (4H, bm), 3.75 (4H, bm), 6.35 (1H, dd), 7.08 (1H, dd), 7.45 (1H, dd)], affords under the same conditions the two possible sulfides in almost equal yields; this dealkylation is therefore a non-regioselective process.

[11] G. A. Cordell, *J. Org. Chem.*, **40**, 3161 (1975); H. M. Gilow and D. E. Burton, *ibid.*, **46**, 2221 (1981).

[12] L. Rasteikiene, D. Greiciute, M. G. Lin'kova and I. L. Knunyants, *Russ. Chem. Rev.*, 548 (1977); E. Kuhle, *Synthesis*, 563 (1971).

[13] L. F. Miller and R. E. Bambury, *J. Med. Chem.*, **13**, 1022 (1970); J. M. Patterson and S. Soedigdo, *J. Org. Chem.*, **33**, 2057 (1968); J. M. Patterson, L. T. Burka and M. R. Boyd, *ibid.*, **33**, 4033 (1968).

[14] C. D. Ritchie and A. L. Pratt, *J. Am. Chem. Soc.*, **86**, 1571 (1964).

[15] A. R. Katritzky and C. W. Rees, Comprehensive Heterocyclic Chemistry, Vol **4**, Part 3, Pergamon Press, London, 1984, p 369.